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Publication number: **0 604 074 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **93309946.7**

(22) Date of filing: **10.12.93**

(51) Int. Cl.<sup>5</sup>: **C08L 67/02, C08K 5/32,  
C08K 5/524, //(C08L67/02,  
67:02)**

(30) Priority: **22.12.92 US 994738**

(43) Date of publication of application:  
**29.06.94 Bulletin 94/26**

(84) Designated Contracting States:  
**DE ES FR GB IT NL**

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(54) **Stabilization of polybutylene terephthalate/polyester blends.**

(57) Blends of low molecular weight PBT resin and high molecular weight polyester resin, such as high molecular weight PBT resin, are imparted with excellent melt viscosity stability by the addition of certain phosphorus-containing compounds.

**EP 0 604 074 A1**

The present invention relates to blends of low molecular weight polybutylene terephthalate resins and high molecular weight polyester resins having improved melt viscosity stability.

## **BACKGROUND OF THE PRESENT INVENTION**

5 Polyester resins derived from terephthalic acid and reactive derivatives thereof, such as dimethylene terephthalate, and alkane diols, e.g., of from 1 to 10 carbon atoms, e.g., ethylene glycol, and 1,4-butanediol, as well as related diols, such as 1,4-cyclohexane dimethanol, and mixtures of such resins have been known for some time and have become important constituents in injection moldable compositions. Workpieces  
10 molded from such polyester compositions, alone, or combined with reinforcements, offer a high degree of surface hardness and abrasion resistance, high gloss, and lower surface friction.

Accordingly, polyesters have found significant commercial applications. Polyesters are effectively used as an engineering plastic for electrical components, machines, cars, sporting goods, interior decorative goods and the like. For many of these applications it is desirable to employ a polyester resin having a  
15 relatively high molecular weight, i.e., having a melt viscosity of above about 600 poise as measured using a Tinius Olsen melt indexer at 250 °C, 0.042 inch orifice (ASTM method D-1238); or having an intrinsic viscosity of above about 0.6 decaliters/gram as measured using a 120-130 mg sample of polyester in a 3:2 mixture of phenol/tetrachloroethane and measuring the time of flow with a Ubbelohde capillary viscometer at 25 °C.

20 However, a problem which many plastics operators have experienced with high molecular weight polyesters is the difficulty in processing the resins. In response thereto, a relatively low molecular weight PBT, less than about 600 poise, as measured using a Tinius Olsen melt indexer at 250 °C, 0.042 inch orifice (ASTM method D-1238) has been added to the high molecular weight polyester to provide improved flow blends which still retain the excellent properties of the high molecular weight polyester. However, it has  
25 been found that while the blends of high molecular weight polyester and low molecular weight PBT initially exhibit a decrease in melt viscosity, the melt viscosity builds over time. See Figure 1. Such a build up of viscosity of the blends limits the use of low molecular weight PBT in commercial applications. It would therefore represent a notable advance in the state of the art if a more stable high flow blend of a high molecular weight polyester and low molecular weight PBT could be found.

30 Jacquiss et al., United States Patent No. 4,532,290, teach stabilizing polycarbonate-polyester compositions against undesirable changes in melting point by adding monosodium phosphate and/or monopotassium phosphate to the compositions. Hepp, United States Patent No. 4,687,802, discloses that the arc track rate of PBT resins can be improved by the addition of a metal salt to the PBT resin.

However, none of the prior art teachings suggests a method of preparing a stable high flow blend of a  
35 high molecular weight polyester and a low molecular weight PBT. Surprisingly, the present inventor has now found that if certain phosphorus-containing compounds are added to the blends of high molecular weight polyester and low molecular weight PBT, there is achieved a high flow blend having excellent melt stability.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

40 FIGURE 1 depicts in graphic form a comparison of a time sweep of the melt viscosity of an unstabilized blend of a high molecular weight PBT (1100 poise) resin and a low molecular weight (300 poise) PBT resin (Line A) against a time sweep of a high molecular weight PBT resin (Line B).

FIGURE 2 depicts in graphic form a comparison of time sweeps of blends of high molecular weight  
45 PBT and low molecular weight PBT with various additives from the data set forth in Table 1 hereinbelow.

## **SUMMARY OF THE PRESENT INVENTION**

According to the present invention there is disclosed a thermoplastic resin blend comprising: (a) a  
50 relatively low molecular weight polybutylene terephthalate resin; (b) a relatively high molecular weight polyester resin; and (c) an effective melt viscosity stabilizing amount of (i) an acidic phosphate salt, (ii) an acid, alkyl, aryl or mixed phosphite having at least one hydrogen or alkyl group, (iii) a Group IB or IIB metal phosphate salt (iv) a phosphorous oxo acid or (v) a mixture of any of the foregoing.

Also according to the present invention there is provided a process for stabilizing the melt viscosity of a  
55 thermoplastic resin blend comprising a relatively low molecular weight PBT resin and a relatively high molecular weight polyester resin comprising adding to the blend an effective amount of (i) an acidic phosphate salt, (ii) an acid, alkyl, aryl or mixed phosphite having at least one hydrogen or alkyl group, (iii) a Group IB or IIB metal phosphate salt (iv) a phosphorous oxo acid or (v) a mixture of any of the foregoing.

**DETAILED DESCRIPTION OF THE PRESENT INVENTION**

The low molecular weight polybutylene terephthalate (PBT) useful in the practice of the present invention is a PBT resin having a melt viscosity of less than 600 poise, more preferably less than about 450 poise, and most preferably less than about 300 poise.

The high molecular weight polyester resins useful in the practice of the present invention are polyester resins having a melt viscosity above about 600 poise, more preferably above about 900 poise, and most preferably above about 1100 poise. Preferred as the high molecular weight polyester resins are high molecular weight polybutylene terephthalate, polyethylene terephthalate and polycyclohexane dimethylene terephthalate.

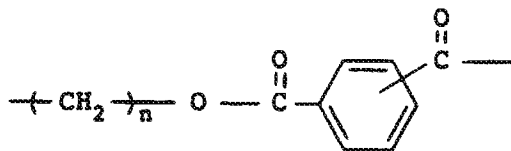
The low molecular weight polybutylene terephthalate resin employed in the present invention is typically one obtained by polymerizing a glycol component at least 70 mol %, preferably at least 80 mol %, of which comprises a tetramethylene glycol; and an acid component at least 70 mol %, preferably at least 80 mol %, of which comprises terephthalic acid, and polyester-forming derivatives thereof. Particularly useful is poly(1,4-butylene terephthalate).

Preferably, the glycol does not contain more than 30 mol %, more preferably not more than 20 mol %, of another glycol, such as ethylene glycol, trimethylene glycol, 2-methyl-1,3-propane glycol, hexamethylene glycol, decamethylene glycol, cyclohexane dimethanol, or neopentylene glycol. Examples of other copolycondensable polyols include 1,3-propylene glycol, pentaerythritol, 1,6-hexanediol, polyethylene glycol and polytetramethylene glycol.

Preferably the acid component contains not more than 30 mol %, more preferably not more than 20 mol %, of another acid such as isophthalic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenoxyethanedicarboxylic acid, p-hydroxy benzoic acid, sebacic acid, adipic acid and polyester-forming derivatives thereof. Examples of other copolycondensable polycarboxylic acids include azelaic acid, dodecane dicarboxylic acid, trimellitic acid, trimesic acid and hexahydroterephthalic acid.

The low molecular weight PBT resins can be prepared according to methods known to those of ordinary skill in the art, or they may be obtained commercially: Low molecular weight PBT is VALOX® 195 having a melt viscosity of about 300 poise from General Electric Company.

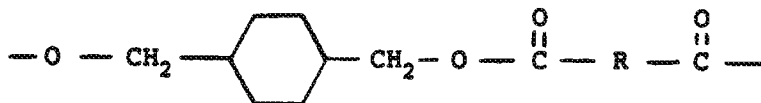
The high molecular weight polyester resins are those which are prepared in similar manner to the low molecular weight PBT, i.e., by polymerizing a glycol component and an acid component. Typically they are derived from an aliphatic or cycloaliphatic diol, or mixtures thereof, containing from 2 to about 10 carbon atoms and at least one aromatic dicarboxylic acid. Preferred polyesters are derived from an aliphatic diol and an aromatic dicarboxylic acid and have repeating units of the following general formula :



wherein n is an integer of from 2 to 6. The most preferred polyesters are poly(ethylene terephthalate), poly(1,4-butylene terephthalate) and mixtures thereof.

Also contemplated for use herein as the high molecular weight polyesters, are the above polyesters with minor amounts, e.g., from 0.5 to about 5 percent by weight, of units derived from aliphatic acids and/or aliphatic polyols to form copolyesters. The aliphatic polyols include glycols, such as poly(ethylene glycol). All such polyesters can be made following the teachings of, for example, United States Patent Nos. 2,465,319 and 3,047,539.

Also useful as the high molecular weight polyesters are those derived from a cycloaliphatic diol and an aromatic dicarboxylic acid and which are prepared, for example, by condensing either the cis- or transomer (or mixtures thereof) of, for example, 1,4-cyclohexanedimethanol with an aromatic dicarboxylic acid so as to produce a polyester having recurring units of the following formula:

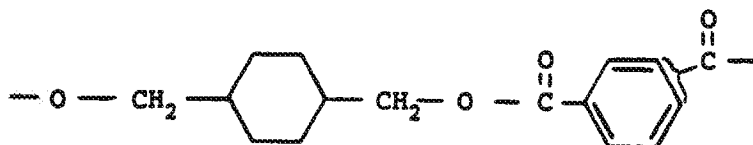


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wherein the cyclohexane ring is selected from the cis- and trans- isomers thereof and R represents an aryl radical containing from 6 to about 20 carbon atoms and which is the decarboxylated residue derived from an aromatic dicarboxylic acid.

10 Examples of aromatic dicarboxylic acids represented by the decarboxylated residue R are isophthalic or terephthalic acid, 1,2-di-(p-carboxyphenyl) ethane, 4,4'-dicarboxydiphenyl ether, etc., and mixtures of these. All of these acids contain at least one aromatic nucleus. Acids containing fused rings can also be present, such as in 1,4- or 1,5-naphthalenedicarboxylic acids. The preferred dicarboxylic acids are terephthalic acid or a mixture of terephthalic and isophthalic acids.

15 Another useful high molecular weight polyester may be derived from the reaction of either the cis- or trans- isomer (or a mixture thereof) of 1,4-cyclohexanedimethanol with a mixture of isophthalic and terephthalic acids. Such a polyester would have repeating units of the formula :

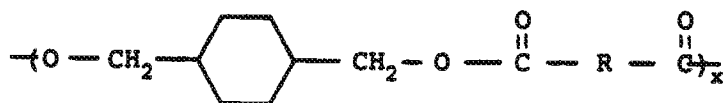


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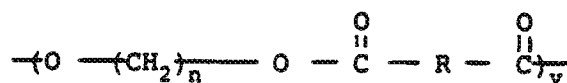
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Still another useful high molecular weight polyester is a copolyester derived from a cyclohexanedimethanol, an alkylene glycol and an aromatic dicarboxylic acid. These copolyesters are prepared by condensing either the cis- or trans- isomer (or mixture thereof) of, for example, 1,4-cyclohexanedimethanol and an alkylene glycol with an aromatic dicarboxylic acid so as to produce a copolyester having units of the formulae:

30



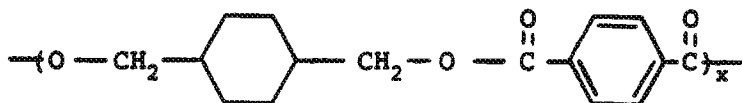
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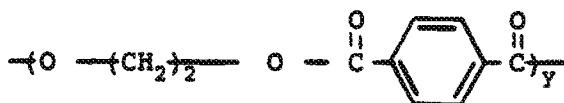
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wherein the cyclohexane ring is selected from the cis- and trans- isomers thereof, R is as previously defined, n is an integer of 2 to 6, the x units comprise from about 10 to about 90 percent by weight and the y units comprise from about 90 to about 10 percent by weight.

45 Such copolyesters may be derived from the reaction of either the cis- or trans- isomer (or mixtures thereof) of 1,4-cyclohexanedimethanol and ethylene glycol with terephthalic acid in a molar ratio of 1:2:3. These copolyesters have repeating units of the following formulae :



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wherein x and y are as previously defined.

The high molecular weight polyesters described herein are either commercially available or can be produced by following methods well known in the art, such as those set forth in, for example, United States Patent Nos. 2,901,466, 2,465,319 and 3,047,539.

5 Particularly suitable for practice of the present invention is high molecular weight PBT, which is sold commercially as VALOX® 295 (melt viscosity of about 1100 poise) or VALOX® 315 (melt viscosity of about 8500 poise), both available from General Electric Company.

The PBT blend can comprise the low molecular weight PBT resin in amounts ranging from about 5 to about 95, preferably from about 20 to about 80, more preferably from about 30 to about 70 and most  
10 preferably from about 40 to about 60 parts by weight based on 100 total parts by weight of the low molecular weight PBT and high molecular weight polyester resins taken together. Accordingly, the PBT blend comprises the high molecular weight polyester resin in amounts ranging from about 95 to about 5, preferably from about 90 to about 10, more preferably from about 70 to about 30 and most preferably from about 60 to about 40, parts by weight based on 100 total parts by weight of the low molecular weight PBT  
15 and high molecular weight polyester resins taken together.

The phosphorus-containing stabilizers of the present invention may comprise (i) acidic phosphate salts such as monozinc phosphates, sodium dihydrogen phosphate, potassium hydrogen phosphate, calcium hydrogen phosphate, sodium acid pyrophosphate and mixtures thereof. It has also been found that certain phosphite compounds (ii) may also be used in the practice of the present invention, e.g., those of the  
20 general formula  $P-(OR')_3$  wherein each R' is the same or different and independently represents hydrogen, alkyl groups, aryl groups or any mixture thereof provided that at least one of the R' groups is hydrogen or alkyl. Illustratively, these include, but are not limited to, diphenylisodecyl phosphite, diisooctyl phosphite, dilauryl phosphite, diphenyl phosphite, phenyl diisodecyl phosphite, ethyl hexyl diphenyl phosphite, stearyl phosphite and mixtures thereof. The phosphorus-containing stabilizers may also comprise (iii) Group IB or  
25 Group IIB phosphate salts such as zinc phosphate or (iv) phosphorous oxo acids such as phosphorous acid, phosphoric acid, polyphosphoric acid, or hypophosphorous acid.

Preferred are phosphorus-containing compounds selected from zinc phosphate, diphenylisodecyl phosphite, monosodium phosphate and sodium acid pyrophosphate and mixtures thereof. Most preferred is zinc phosphate.

30 The phosphorus-containing compounds are generally employed in the compositions of the present invention in amounts ranging from about 0.1 to about 10, preferably from about 0.1 to about 5, more preferably from about 0.1 to about 2 and most preferably from about 0.2 to about 1, weight percent based on the weight of the total composition.

The compositions of the present invention may also comprise other thermoplastic resins which are  
35 conventionally added to polyester resins. These may include resins such as polycarbonates, polyester-carbonates, polyarylates and mixtures thereof.

In other embodiments of the present invention, the compositions can further comprise impact modifiers. Particularly useful impact modifiers generally comprise rubbery impact modifiers. These are well known to those skilled in the art, and any of them normally employed with polyester resins may be employed herein.

40 The preferred impact modifiers generally comprise an acrylic or methacrylic grafted polymer of a conjugated diene or an acrylate elastomer, alone, or copolymerized with a vinyl aromatic compound. Particularly useful are the core-shell polymers of the type available from Rohm & Haas, for example, those sold under the trade designation Acryloid®. In general these impact modifiers contain units derived from butadiene or isoprene, alone or in combination with a vinyl aromatic compound, or butyl acrylate, alone or  
45 in combination with a vinyl aromatic compound. The aforementioned impact modifiers are believed to be disclosed in Fromuth et al., United States Patent No. 4,180,494; Owens, United States Patent No. 3,808,180; Farnham et al., United States Patent No. 4,096,202; and Cohen et al., United States Patent No. 4,260,693. Most preferably, the impact modifier will comprise a two stage polymer having either a butadiene or butyl acrylate based rubbery core and a second stage polymerized from methylmethacrylate alone, or in  
50 combination with styrene. Also present in the first stage are crosslinking and/or graftlinking monomers. Examples of the crosslinking monomers include 1,3-butylene diacrylate, divinyl benzene and butylene dimethacrylate. Examples of graftlinking monomers are allyl acrylate, allyl methacrylate and diallyl maleate.

Additional preferred impact modifiers are of the type disclosed in United States Patent No. 4,292,233. These impact modifiers comprise, generally, a relatively high content of a cross-linked butadiene polymer  
55 grafted base having grafted thereon acrylonitrile and styrene.

Other suitable impact modifiers include, but are not limited to ethylene vinyl acetate, ethylene ethylacrylate copolymers, SEBS (styrene ethylene-butylene styrene) and SBS (styrene-butadiene-styrene) block copolymers, EPDM (ethylene propylene diene monomer) and EPR (ethylene propylene rubber)

copolymers, etc. All of these are well known to those skilled in the art and are available commercially.

The compositions of the present invention may further contain one or more reinforcing agents including glass fibers. Typical reinforcing agents useful in the practice of the present invention include, but are not limited to, glass fiber, talc, mica, clay or combinations thereof.

5 The filamentous glass which may be employed as a reinforcing agent in the present compositions is well known to those skilled in the art and is widely available from a number of manufacturers. For compositions to be employed for electrical uses, it is preferred to use fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively soda-free. This is more commonly known as "E" glass. However, other glasses are useful where electrical properties are not so important, e.g., the low soda glass  
10 known as "C" glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. The filament diameters generally range from about 0.00012 to 0.00075 inches but this is not critical to the present invention.

Further, the glass fibers useful in the practice of the present invention may also be treated with functionalized silicon compounds to improve interaction with the polymer matrix, as is well known to those  
15 skilled in the art. Functionalized silanes, especially alkoxy silanes may be useful in this regard. Illustratively these include, but are not limited to, aminopropyl triethoxy silane, glycidyl propyl trimethoxy silane, (3,4-epoxy cyclohexyl) ethyl triethoxy silane, mercaptopropyl silane, aminoethyl aminopropyl alkoxy silane, ureido-alkyl trialkoxy silane and mixtures of any of the foregoing.

The length of the glass filaments and whether or not they are bundled into fibers and the fibers bundled  
20 in turn to yarns, ropes or rovings, or woven into mats and the like are also not critical to the present invention. However, in preparing molding compositions it is convenient to use the filamentous glass in the form of chopped strands of from about 0.0125 to about 2 inches long. In articles molded from the compositions on the other hand, even shorter lengths will be encountered due to fragmentation during compounding.

25 In general, the filamentous glass reinforcement comprises from about 2.5 to about 60% by weight based on the total weight of the compositions of the present invention. It is more preferred that the glass comprise from about 5 to about 55 and most preferred from about 20 to about 40% by weight of the total weight of the composition.

The present invention may further comprise a flame retardant compound. Any of the conventional  
30 halogenated aromatic flame retardants such as decabromodiphenyl ether, brominated phthalimides, brominated polyphenylene ethers, bromine containing polyacrylates or methacrylates, i.e., polypentabromobenzyl acrylate and/or brominated styrene polymers can be employed in the present invention. These are well known to those skilled in the art and are described in the patent literature. Preferred are derivatives of tetrabromo bisphenol A, such as its polycarbonate polymer or the polymer of its adduct with  
35 epichlorohydrin (brominated phenoxy resin). They may be used alone, or in conjunction with a synergist, particularly inorganic or organic antimony compounds. Such compounds are widely available or can be made in known ways. Especially preferred is antimony oxide.

Flame retardant embodiments of the present invention may further comprise a drip retardant agent to prevent dripping during burning. Such compounds are well known to those skilled in the art and include, but  
40 are not limited to, various fluorinated polyolefins. Particularly useful is polytetrafluoroethylene (PTFE). See, e.g., Wambach, United States Patent No. 3,671,487.

The compositions of the present invention can also comprise a wide variety of other additives, such as UV stabilizers, pigments, colorants, fillers, plasticizers, processing aids, antioxidants and the like. Such components are added in effective amounts to impart the desired properties on the compositions of the  
45 present invention for the specific application.

The method of blending the compositions of the present invention is not critical and can be carried out by conventional melt processing techniques. One convenient method comprises blending the PBT resins and other ingredients in powder or granular form, extruding the blend and comminuting into pellets or other  
50 suitable shapes. The ingredients are combined in any usual manner, e.g., by dry mixing or by mixing in the melted state in an extruder, on a heated mill or in other mixers.

An alternative method of blending can comprise preparing a preblend of the polyesters and then adding the other ingredients to the preblend. For example, a preblend of the PBT resins and stabilizer can be fed into the upstream port of an extruder with addition of the other ingredients such as glass fibers in a downstream port of the extruder.

55 In another embodiment, the various compounds can be precompounded, pelletized and then molded. Precompounding can be carried out in conventional equipment. For example, a dry blend of the ingredients can be fed into a single screw extruder, the screw having a long transition section to insure proper melting. Alternatively, a twin screw extrusion machine can be fed with the resins and other additives at the feed port

and reinforcements fed downstream. In either case, a generally suitable machine temperature will be from about 450° to about 575° F.

The precompounded composition can be extruded and cut or chopped into molding compounds, such as conventional granules, pellets, etc. by standard techniques.

- 5 The compositions can be molded in any equipment conventionally used for thermoplastic compositions. For example, good results will be obtained in an injection molding machine, with conventional cylinder temperatures, e.g., 500° F, and conventional mold temperatures, e.g., 150° F.

#### **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

10

The following examples are presented in order to illustrate the present invention. They are not to be construed to limit the scope of the appended claims in any manner whatsoever.

#### **EXAMPLES 1-3**

15

The following examples demonstrate the use of various stabilizers in a polyester resin blend. The blends are prepared by tumble blending the ingredients (parts by weight), extruding in a 2.5 inch vented single screw extruder with a melt temperature of 500 to 530° F. They are dried and molded on an 80 ton Van Dorn injection molding machine at a temperature of 500° C, and a mold temperature of 150° C.

20 Kayness® melt viscosity is measured by predrying the sample for 1 hour in a circulating oven at 150° C and using a Kayness, Galaxy V capillary rheometer with a melt temperature of 250° C, melt force of 150 lbs, and a shear rate of 400 sec<sup>-1</sup>. Parallel plate rheology is measured using a Gottfert® 2001 rheometer with a parallel plate radius of 12.5 mm, a gap of 1.0 mm and a melt temperature of 250° C with a 15% strain. The results along with compositional data are set forth below in Table 1.

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TABLE 1

Example	1A*	1	2	3
Composition, pbw				
PBT 295 <sup>a</sup>	40	40	40	40
PBT 195 <sup>b</sup>	15	15	15	15
Glass fibers <sup>c</sup>	30	30	30	30
FRC <sup>d</sup>	13.2	13.2	13.2	13.2
PTFE <sup>e</sup>	1.25	1.25	1.25	1.25
Irganox 1076 <sup>f</sup>	0.15	0.15	0.15	0.15
PE-18 <sup>g</sup>	0.2	0.2	0.2	0.2
DPDP <sup>h</sup>	--	0.2	--	--
ZnP <sup>i</sup>	--	--	0.2	--
SAPP <sup>j</sup>	--	--	--	0.2
Properties				
Viscosity, poise <sup>k</sup> Rheology				
1 minute	5434	4509	4201	5434
15 minutes	7647	6649	6325	6375
% increase	41	47	51	17
30 minutes	14610	7423	7099	12450
% increase	169	64	69	129

\* = Comparative Example

<sup>a</sup> = Valox® 295, General Electric Company, 1100 poise

<sup>b</sup> = Valox ® 195, General Electric Company, 300 poise

<sup>c</sup> = OCF 183E, K filament glass, Owens Corning Fiberglass

<sup>d</sup> = Flame retardant concentrate of brominated polycarbonate, antimony oxide, and a polymer binder

<sup>e</sup> = Polytetrafluoroethylene resin dispersion

<sup>f</sup> = Antioxidant, Ciba-Geigy Company

<sup>g</sup> = Pentaerythritol tetrastearate

<sup>h</sup> = Diphenylisodecyl phosphite, GE Specialty Chemical

<sup>i</sup> = Zinc phosphate, Alfa Chemical Company

<sup>j</sup> = Sodium acid pyrophosphate

<sup>k</sup> = Measured by parallel plate rheology at 250 °C

A time sweep of the melt viscosity for the above examples is shown in Figure 2. It can be seen that the compositions stabilized with DPDP, ZnP and SAPP exhibit significantly improved melt viscosity stability over the control example.

#### EXAMPLES 4-5

The procedure of Example 1 is generally followed to illustrate the effectiveness of zinc phosphate as a melt stabilizer in polyester blends. The results, along with compositional data are set forth in Table 2 below.



TABLE 2

Example	4A*	4	5A*	5
Composition, pbw				
PBT 195 <sup>a</sup>	50	49.8	50	49.8
PBT 295 <sup>b</sup>	50	49.8	--	--
PBT 315 <sup>c</sup>	--	--	50	49.8
ZnP <sup>d</sup>	--	0.4	--	0.4
Properties				
Viscosity, poise Kayeness <sup>e</sup>				
T5 <sup>f</sup>	547	577	1518	1662
T10 <sup>g</sup>	528	544	1303	1439
Rheology <sup>h</sup>				
1 minute	581	610	1589	1868
15 minute	756	676	1554	1530
% increase	30	10.8	-2	-18
30 minute	1109	874	1891	1634
% increase	91	43	19	-12.5

\* = Comparative example

<sup>a</sup> = Valox® 195, General Electric Company, 300 poise

<sup>b</sup> = Valox® 295, General Electric Company, 1100 poise

<sup>c</sup> = Valox® 315, General Electric Company, 8500 poise

<sup>d</sup> = Zinc phosphate,  $Zn_3(PO_4)_2 \cdot 2H_2O$ , Alpha Chem. Co.

<sup>e</sup> = at 250 °C, poise

<sup>f</sup> = dwell time, 5 minutes

<sup>g</sup> = dwell time, 10 minutes

<sup>h</sup> = Parallel plate rheology, viscosity vs. time at 250 °C poise, % viscosity increase from 1 minute

It can be seen from the data in Table 2 that zinc phosphate prevents build up of melt viscosity in the polyester blends, exhibiting a significant improvement in maintaining a consistent melt viscosity over time.

#### EXAMPLE 6

The procedure of Example 1 is followed to compare the effectiveness of zinc phosphate stabilizer over other stabilizers. The results, along with compositional data are set forth below in Table 3.

TABLE 3

Example	6A*	6B*	6C*	6
Composition, pbw				
PBT 295 <sup>a</sup>	40.2	40.2	40.2	40.2
PBT 195 <sup>b</sup>	15.0	15.0	15.0	15.0
Glass Fibers <sup>c</sup>	30.0	30.0	30.0	30.0
FRC <sup>d</sup>	13.2	13.2	13.2	13.2
PTFE <sup>e</sup>	1.25	1.25	1.25	1.25
Irganox 1076 <sup>f</sup>	0.15	0.15	0.15	0.15
PE-18 <sup>g</sup>	0.20	0.20	0.20	0.20
Irgafos 168 <sup>h</sup>	--	0.20	--	--
TPPP <sup>i</sup>	--	--	0.20	--
ZnPi <sup>j</sup>	--	--	--	0.20
Properties				
Viscosity, poise Kayeness <sup>k</sup>				
T5 <sup>l</sup>	2995	3290	3380	2200
T10 <sup>m</sup>	3311	4144	3411	2149
Rheology <sup>n</sup> , poise				
1 min	5183	4636	4414	4044
15 min	10910	7112	7718	5165
% <sup>o</sup>	110	53.4	75	28
30 min	11840	9853	8445	5644
% <sup>o</sup>	128	112	91	40

\* = Comparative Example

<sup>a</sup> = Valox® 295, General Electric Company, 1100 poise<sup>b</sup> = Valox® 195, General Electric Company, 300 poise<sup>c</sup> = OCF 183E, K filament glass, Owens Corning Fiberglass<sup>d</sup> = Flame retardant concentrate, PPG Industries<sup>e</sup> = Polytetrafluoroethylene concentrate<sup>f</sup> = Antioxidant, Ciba Geigy Company<sup>g</sup> = Pentaerythritol tetrastearate<sup>h</sup> = Tris(2,4-di-t-butylphenyl)phosphite, Ciba Geigy Co.<sup>i</sup> = Tetrapotassium pyrophosphate<sup>j</sup> = Zinc phosphate, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O, Alpha Chem. Co.<sup>k</sup> = at 250 °C, poise<sup>l</sup> = dwell time, 5 minutes<sup>m</sup> = dwell time, 10 minutes<sup>n</sup> = Parallel plate rheology, viscosity vs. time at 250 °C<sup>o</sup> = % viscosity increase from 1 minute

Table 3 above clearly demonstrates the improvements in melt viscosity stability obtained with the stabilizers of the present invention. The parallel plate rheology shows a 100% increase in melt viscosity in compositions stabilized with other phosphorus-containing additives, Examples 6A\*-6C\*, while the composition stabilized according to the present invention exhibits less than 50% increase in melt viscosity. Further, the Kayeness data highlights the viscosity increases for the compositions containing other phosphorus-containing additives.

**EXAMPLE 7**

The procedure of Example 1 is generally followed to observe the melt viscosity stability of unfilled polyester blends with various stabilizers. The results, along with compositional data are set forth below in Table 4.

TABLE 4

Example	7A*	7B*	7
Composition, pbw			
PBT 295 <sup>a</sup>	50.0	49.8	49.8
PBT 195 <sup>b</sup>	50.0	49.8	49.8
Irgafos® 168 <sup>c</sup>	--	0.4	--
ZnP <sup>d</sup>	--	--	0.4
Properties			
Viscosity, poise Kayeness <sup>e</sup>			
T5 <sup>f</sup>	539	544	577
T10 <sup>g</sup>	513	508	544
Rheology <sup>h</sup>			
1 min	607	590	610
15 min	828	812	676
% <sup>i</sup>	36	38	11
30 min	1197	1114	874
% <sup>i</sup>	97	89	43

\* = Comparative Example

<sup>a</sup> = Valox® 295, General Electric Company, 1100 poise<sup>b</sup> = Valox® 195, General Electric Company, 300 poise<sup>c</sup> = Tris(2,4-di-t-butylphenyl)phosphite, Ciba Geigy Co.<sup>d</sup> = Zinc phosphate, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O, Alpha Chem. Co.<sup>e</sup> = at 250 ° C, poise<sup>f</sup> = dwell time, 5 minutes<sup>g</sup> = dwell time, 10 minutes<sup>h</sup> = Parallel plate rheology, viscosity vs. time at 250 ° C<sup>i</sup> = % viscosity increase from 1 minute

The data in Table 4 demonstrates the significant improvements obtained according to the present invention in unfilled PBT blends.

#### EXAMPLES 8-13

The procedure of Example 1 is generally followed, except employing further stabilizers. The results, along with compositional data are set forth below in Table 5.

TABLE 5

Example	8A*	8	9	10	11	12	13
Composition, pbw							
Blend <sup>a</sup>	100	99.7	99.4	99.7	99.4	99.7	99.4
ZnP <sup>b</sup>	--	0.3	0.6	--	--	--	--
SAPP <sup>c</sup>	--	--	--	0.3	0.6	--	--
SDP <sup>d</sup>	--	--	--	--	--	0.3	0.6
Properties							
Viscosity, poise							
Kayenex <sup>e</sup>							
T5	2968	2267	2250	2536	2631	2566	--
T10 <sup>g</sup>	3374	2276	2204	2686	2691	2754	2724
Rheology <sup>h</sup>							
1 min.	5320	3713	3725	4452	3994	4421	3991
15 min.	9366	5281	4969	5488	4828	4793	4731
% <sup>i</sup>	76	42	33	23	21	8.4	19
30 min.	12210	5901	5664	8106	6265	7809	5816
% <sup>i</sup>	130	59	52	82	57	76	46

\* = Comparative Example

a = PBT 295 (40.2), PBT 195 (15), glass fiber (30), FRC (13.2), PTFE dispersion (1.25), Irganox® 1076 (0.15), PE-18 (0.2)

b = Zinc phosphate, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O, Alpha Chemical Co.

c = Sodium acid pyrophosphate

d = Monosodium phosphate

e = at 250°C, poise

f = dwell time, 5 minutes

g = dwell time, 10 minutes

h = Parallel plate rheology, viscosity vs. time at 250°C

i = % viscosity increase from 1 minute

The data in Table 5 show the improvements in melt viscosity stability provided by compositions of the present invention.

## EXAMPLES 14-19

The procedure of Example 1 is generally followed, except employing blends of the low molecular weight PBT with polycarbonate in a non-flame retardant system. The results, along with compositional data are set forth below in Table 6.

TABLE 6		14	15	16	17	18	19
Example	14A*						
<b>Composition</b>							
PBT 295 <sup>a</sup>	33.45	33.25	33.15	33.25	33.15	33.25	33.15
PBT 195 <sup>b</sup>	15.0	15.0	15.0	15.0	15.0	15.0	15.0
PC <sup>c</sup>	20.0	20.0	20.0	20.0	20.0	20.0	20.0
SAC <sup>d</sup>	1.55	1.55	1.55	1.55	1.55	1.55	1.55
Zn <sup>e</sup>	--	0.2	0.4	--	--	--	--
SAPP <sup>f</sup>	--	--	--	0.2	0.4	--	--
DPDP <sup>g</sup>	--	--	--	--	--	0.2	0.4
<b>Properties</b>							
<b>Viscosity<sup>h</sup></b>							
Kayenes <sup>i</sup>							
T5 <sup>j</sup>	4670	3867	3482	3287	3326	3375	3457
T10 <sup>j</sup>	6252	5072	4190	3277	3298	3311	3413
%	34	31	27	-0.3	-0.8	-1.9	-1.3

\* = Comparative Example

a = Valox® 295, General Electric Company, 1100 poise

b = Valox® 195, General Electric Company, 300 poise

c = Poly(bisphenol A) carbonate, General Electric Company

d = Mold release/antioxidant stabilizer concentrate

e = Zinc phosphate, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O, Alpha Chem. Co.

f = Sodium acid pyrophosphate

g = diphenylisododecyl phosphite, GE Specialty Chemical

h = at 250°C, poise

i = dwell time, 5 minutes

j = dwell time, 10 minutes

The above-mentioned patents and test methods are all hereby incorporated by reference.

Many variations of the present invention will suggest themselves to those of ordinary skill in the art in light of the above-detailed description. Conventional additives such as clay, mica, pigments and colorants can be added in conventional amounts. Other phosphite stabilizers such as diisooctyl phosphite, triauryl phosphite, diphenyl phosphite, phenyl diisodecyl phosphite, ethyl hexyl diphenylphosphite and stearyl phosphite may be employed. Further, the compositions can include a wide variety of other thermoplastic resins such as polycarbonates, polyarylates, polyester carbonates and mixtures thereof; as well as a variety of impact modifiers such as core-shell polymers, ethylene vinyl acetate, ethylene ethylacrylate copolymer, SEBS, SBS, EPDM and EPR. All such obvious variations are within the full intended scope of the appended claims.

10

## Claims

1. A thermoplastic resin blend comprising:
  - (a) a relatively low molecular weight polybutylene terephthalate resin;
  - (b) a relatively high molecular weight polyester resin; and
  - (c) an effective melt viscosity stabilizing amount of (i) an acidic phosphate salt, (ii) an acid, alkyl, aryl or mixed phosphite having at least one hydrogen or alkyl group, or (iii) a Group IB or IIB metal phosphate salt, (iv) a phosphorous oxo acid or (v) a mixture of any of the foregoing.
2. A thermoplastic resin blend as defined in Claim 1 wherein said component (a) has a melt viscosity of less than 600 poise.
3. A thermoplastic resin blend as defined in Claim 2 wherein said component (a) has a melt viscosity of less than about 450 poise.
4. A thermoplastic resin blend as defined in Claim 1 wherein said component (b) has a melt viscosity of greater than about 800 poise.
5. A thermoplastic resin blend as defined in Claim 1 wherein said component (b) has a melt viscosity of greater than about 900 poise.
6. A thermoplastic resin blend as defined in Claim 1 wherein said component (a) comprises a poly(1,4-butylene terephthalate) resin.
7. A thermoplastic resin blend as defined in Claim 1 wherein said component (b) comprises a poly(1,4-butylene terephthalate) resin.
8. A thermoplastic resin blend as defined in Claim 1 wherein said component (b) comprises polyethylene terephthalate, polycyclohexane dimethylene terephthalate or a mixture thereof.
9. A thermoplastic resin blend as defined in Claim 1 wherein said acidic phosphate salt component (c)(i) is selected from zinc monophosphate, monosodium phosphate, sodium acid pyrophosphate and mixtures of any of the foregoing.
10. A thermoplastic resin blend as defined in Claim 1 wherein said phosphite component (c)(ii) comprises a phosphite of the general formula
 
$$P-(OR')_3$$
 wherein each R' is the same or different and independently represents hydrogen, alkyl, aryl or a mixture of alkyl and aryl provided that at least one R' group is hydrogen or alkyl.
11. A thermoplastic resin blend as defined in Claim 10 wherein said phosphite component (c)(ii) is selected from the group of diisooctyl phosphite, triauryl phosphite, diphenyl phosphite, phenyl diisodecyl phosphite, ethyl hexyl diphenyl phosphite, stearyl phosphite and mixtures of any of the foregoing.
12. A thermoplastic resin blend as defined in Claim 11 wherein said phosphite component (c)(ii) comprises diphenylisodecyl phosphite.

13. A thermoplastic resin blend as defined in Claim 1 wherein said component (c)(iii) comprises zinc phosphate.
14. A thermoplastic resin blend as defined in Claim 1 wherein said phosphorous oxo acid (c)(iv) comprises phosphorous acid, phosphoric acid, polyphosphoric acid, hypophosphorous acid or mixtures thereof.
15. A thermoplastic resin blend as defined in Claim 1 comprising from about 30 to about 70 parts by weight component (a), from about 70 to about 30 parts by weight component (b), and from about 0.1 to about 10 parts by weight component (c) based on 100 total parts by weight of components (a), (b) and (c).
16. A thermoplastic resin blend as defined in Claim 1 further comprising (d) a thermoplastic resin selected from polycarbonates, polyester carbonates, polyarylates and mixtures of any of the foregoing.
17. A thermoplastic resin blend as defined in Claim 16 wherein said component (d) comprises a poly-(bisphenol A) carbonate.
18. A thermoplastic resin blend as defined in Claim 1 further comprising (e) a reinforcing agent comprising glass fibers, talc, mica, clay or mixtures thereof.
19. A thermoplastic resin blend as defined in Claim 1 further comprising (f) a flame retardant agent.
20. A thermoplastic resin blend as defined in Claim 1 further comprising (g) an additive selected from impact modifiers, pigments, fillers, plasticizers, processing aids, UV stabilizers, antioxidants and mixtures of any of the foregoing.
21. An article prepared from a composition as defined in Claim 1.
22. A process for stabilizing the melt viscosity of a thermoplastic resin blend comprising a relatively low molecular weight PBT and a relatively high molecular weight polyester, said process comprising adding to said blend an effective amount of a phosphorus compound comprising (i) an acidic phosphate salt, (ii) an acid, alkyl, aryl or mixed phosphite having at least one hydrogen or alkyl group, (iii) a Group IB or IIB metal phosphate salt, (iv) a phosphorous oxo acid or (v) a mixture of any of the foregoing.
23. A process as defined in Claim 22 wherein said relatively low molecular weight PBT resin has a melt viscosity of less than about 450 poise and said relatively high molecular weight polyester resin has a melt viscosity of greater than about 900 poise.
24. A process as defined in Claim 23 wherein said high molecular weight polyester resin comprises polybutylene terephthalate, polyethylene terephthalate, polycyclohexane dimethylene terephthalate, or a mixture of any of the foregoing.
25. A process as defined in Claim 22 wherein said phosphorus compound is selected from the group consisting of zinc phosphate, diphenylisodecyl phosphite, monosodium phosphate, sodium acid pyrophosphate and mixtures of any of the foregoing.
26. A thermoplastic resin blend as defined in Claim 25 wherein said phosphorus component comprises zinc phosphate.
27. A thermoplastic resin blend having improved melt viscosity stability consisting essentially of
  - (a) a low molecular weight polybutylene terephthalate resin;
  - (b) a high molecular weight polyester resin; and
  - (c) an effective melt viscosity stabilizing amount of (i) an acidic phosphate salt, (ii) an acid, alkyl, aryl or mixed phosphite having at least one hydrogen or alkyl group, (iii) a Group IB or IIB metal phosphate salt, (iv) a phosphorous oxo acid or (v) a mixture of any of the foregoing; and, optionally, one or more of the following components:
  - (d) a thermoplastic resin selected from polycarbonates, polyester carbonates, polyarylates and mixtures of any of the foregoing;

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- (e) a reinforcing agent;
- (f) a flame retardant agent; and
- (g) an additive selected from impact modifiers, pigments, fillers, colorants, plasticizers, processing aids, UV stabilizers, antioxidants and mixtures of any of the foregoing.

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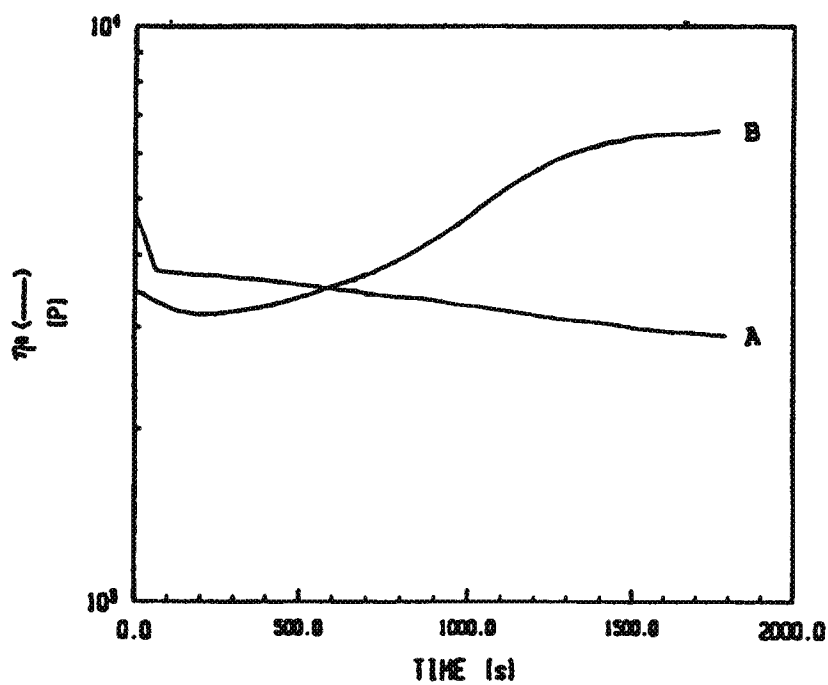
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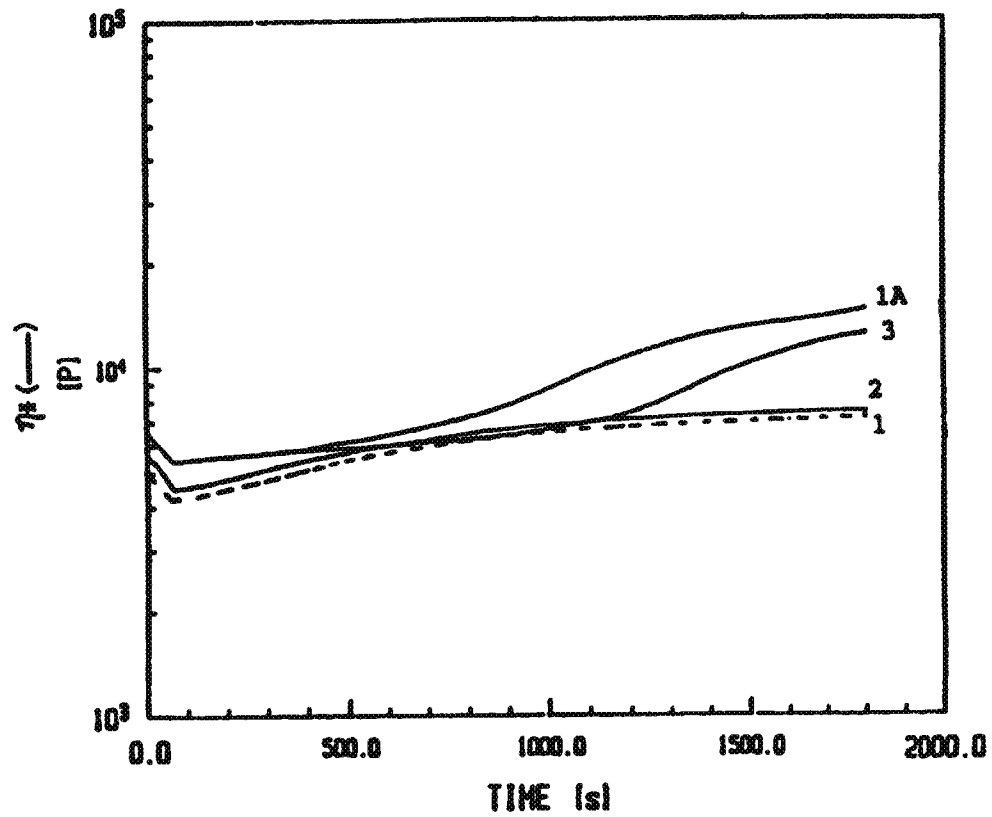
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**FIGURE 1**  
**TIME SWEEP, 250°C**  
**PBT BLENDS, NO STABILIZER**



**FIGURE 2**  
**TIME SWEEP, 250°C**  
**STABILIZED PBT BLENDS**





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 93 30 9946

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claims	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	EP-A-0 362 872 (SUMITOMO WIRING SYSTEMS, LTD) * claims 1-13 * ---	1-8, 10, 15, 21-24	C08L67/02 C08K5/32 C08K5/524 //(C08L67/02, 67:02)
Y	US-A-2 437 046 (ROTHROCK ET AL) * claims 1-7 * ---	1-8, 10, 15, 21-24	
A	US-A-4 972 015 (CARICO ET AL) * column 1, line 55 - column 2, line 9; claim 1 * ---	1, 9	
A	EP-A-0 172 115 (RHONE-POULENC SPECIALITES CHIMIQUES) * claims 1-7 * ---	1	
P, A	EP-A-0 552 546 (GE PLASTICS JAPAN LIMITED) * abstract * ---	1	
D, A	US-A-4 532 290 (JAQUISS ET AL) * claim 1 * -----	1, 9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C08L C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 March 1994	Examiner Decocker, L
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPF FORM 1503 (03.92) (P/NCB)



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Publication number: **0 414 944 A1**

12

## EUROPEAN PATENT APPLICATION

21 Application number: **89116089.7**

22 Date of filing: **31.08.89**

51 Int. Cl.<sup>5</sup>: **C08L 69/00, C08L 79/08,  
C08K 3/32, C08L 67/02,  
/(C08L79/08,69:00,C08K3:32),  
(C08L79/08,69:00,67:02,  
C08K3:32)**

43 Date of publication of application:  
**06.03.91 Bulletin 91/10**

84 Designated Contracting States:  
**DE FR GB IT NL**

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54 **Stabilized polycarbonate-polyetherimide ester compositions.**

57 Compositions comprising a polycarbonate resin, e.g., poly(bisphenol A carbonate) and a polyetherimide ester resin are melt stabilized with monosodium phosphate and/or monopotassium phosphate.

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**STABILIZED POLYCARBONATE-POLYETHERIMIDE ESTER COMPOSITIONS**

This invention related generally to polycarbonate-polyetherimide ester resin compositions, alone, or in further combination with other resins, and more particularly to methods for stabilizing blends of high molecular weight thermoplastic polycarbonates and polyetherimide esters against undesirable changes in melting point.

5

**BACKGROUND OF THE INVENTION**

10 Polyetherimide ester elastomers comprised of the reaction products of (a) a low molecular weight diol, (b) a dicarboxylic acid, (c) a high molecular weight poly(oxy alkylene)diamine, and (d) a tricarboxylic acid or its derivative are known and are described in U.S. Patent Nos. 4,544,734 and 4,556,705 to McCready and in U.S. Patent No. 4,556,688 to McCready et al. These polyetherimide esters exhibit excellent stress-strain properties, low tensile set, high melting temperatures and/or excellent strength/toughness characteristics as well as superior flexibility, which properties render said polyetherimide esters especially suitable for molding and extrusion applications.

15 Blends of such polyetherimide ester resins with one or more second resins have become of significant commercial interest because such second resins, carefully selected, can improve certain physical properties of the polyetherimide ester resins. By way of illustration, such second resins can comprise aromatic polycarbonate resins.

20 Polycarbonate-polyetherimide ester resin compositions are disclosed in copending Patent Application Serial Number . It has been discovered that these compositions alone, or in combination with other resins, have, however, a tendency to be unstable in the molten states as evidenced by a change in melting point.

25 It has now been discovered that two specific inorganic phosphorus reagents, monosodium phosphate and monopotassium phosphate, alone, or in combination, are highly effective to stabilize such polycarbonate-polyetherimide ester resin compositions containing, predominantly, polycarbonate, especially if the polyetherimide ester is made with a titanium compound catalyst, e.g., tetra octyl titanate. Monosodium phosphate and monopotassium phosphate, both rather innocuous, mildly acidic reagents, are surprisingly effective as stabilizers for polycarbonate-polyetherimide ester compositions. The stabilizers can be used in various manners, including prior incorporation as a concentrate in the polycarbonate resin, or in the polyetherimide ester resin. In addition to the high degree of reliability as stabilizers in such compositions, monosodium phosphate and/or monopotassium phosphate do not detrimentally affect any of the resinous components in the composition, e.g., the polycarbonates, or the polyetherimide ester.

30 Also difficult to melt stabilize are combinations of polycarbonates and polyetherimide ester resins with third resins such as polyolefin terephthalates. Such formulations are rendered reliably melt stable with monosodium phosphate and/or monopotassium phosphate, according to the present invention. In addition to the specific instances noted above, melt stabilization can also be induced in other combinations of polycarbonates with polyetherimide ester and other resins, especially those in which an active catalyst was used to prepare one or all of the polymers in the blend.

40

**SUMMARY OF THE INVENTION**

45

Accordingly to the present invention, there are provided thermoplastic compositions comprising a polycarbonate and at least one polyetherimide ester resin, or in further combination with at least one additional resin, melt stabilized with monosodium phosphate and/or monopotassium phosphate.

50

**DESCRIPTION OF THE INVENTION**

Any amount of the monosodium and/or monopotassium phosphate will melt stabilize a polycarbonate-polyetherimide ester resin blend. Preferably, however, from about 0.01 parts to about 7.5 parts by weight of

the phosphate should be used, and most preferably, from about 0.1 parts to about 4.0 parts by weight should be used, based on 100 parts by weight of the total polyetherimide ester resinous component in the composition. Although the phosphates are, as mentioned, relatively innocuous, amounts larger than about 10.0 parts by weight should be used with caution since such larger amounts will provide melt stability, but might also deleteriously affect the mechanical properties of one or more of the resins in the composition.

The phosphate of the invention may be mixed with the polymers by any suitable means. Since most phosphates are solids, they can be most expeditiously mixed with the resin either as a precompounded concentrate, or directly into the melt, e.g., in an extruder.

The polyetherimide ester elastomers utilized in the invention contain imide groups, polyether groups, and ester groups in the polymer chain. They are comprised of the reaction products of:

(i) at least one diol;

(ii) at least one carboxylic acid or its ester forming reactive derivative; and

(iii) a set of reactants selected from

(a) (1) at least one high molecular weight poly(oxy alkylene)diamine, and (2) at least one tricarboxylic acid or its derivative, or

(b) at least one high molecular weight polyoxyalkylene diimide diacid.

Suitable diols (i) for use in the preparation of the polyetherimide ester polymers of the present invention include the saturated and unsaturated aliphatic and cycloaliphatic dihydroxy compounds as well as the aromatic dihydroxy compounds. These diols are preferably of a low molecular weight, i.e., having a molecular weight of about 250 or less. When used herein, the term "diol" and "low molecular weight diol" should be construed to include equivalent ester forming derivatives thereof provided, however, that the aforementioned molecular weight requirement pertains to the diols only and not to their ester forming derivatives. Exemplary of ester forming derivatives of diols there may be given the acetates of the diols as well as, for example, ethylene oxide or ethylene carbonate for ethylene glycol.

The preferred saturated and unsaturated aliphatic acid cycloaliphatic diols are those having from 2 to about 15 carbon atoms. Especially preferred are 1,4-butanediol and mixtures thereof with hexanediol, 1,4-cyclohexane dimethanol, or butanediol, most preferably 1,4-butanediol.

Aromatic diols suitable for use in the practice of the present invention are generally those having from 6 to about 15 carbon atoms.

Especially preferred diols are the saturated aliphatic diols, mixtures thereof, and mixtures of a saturated diol(s) with an unsaturated diol(s), wherein each diol contains from 2 to about 8 carbon atoms. Where more than one diol is employed, it is generally preferred that at least about 80 mole %, based on the total diol content, be the same diol, more preferably at least 80 mole %. As mentioned above, the preferred compositions are those in which 1,4-butanediol is present in a predominant amount, most preferably when 1,4-butanediol is the only diol.

Dicarboxylic acids (ii) which are suitable for use in the practice of the present invention are aliphatic, cycloaliphatic and/or aromatic dicarboxylic acids. These acids are preferably of a low molecular weight, i.e., having a molecular weight of less than about 300. However, in some cases higher molecular weight dicarboxylic acids may be used. The term "dicarboxylic acids" as used herein, includes equivalents of dicarboxylic acids having two functional carboxyl groups which perform substantially like dicarboxylic acids in reaction with glycols and diols in forming polyesters. These equivalents include esters and ester forming reactive derivatives, such as acid halides and anhydrides. The molecular weight preference mentioned above pertains to the acid and not to its equivalent ester or ester-forming derivatives. Thus, an ester of dicarboxylic acid having a molecular weight greater than about 300 or an acid equivalent of dicarboxylic acid having a molecular weight greater than about 300 are included provided the acid has a molecular weight below about 300. Additionally, the dicarboxylic acids may contain any substituent group(s) or combinations which do not substantially interfere with the polymer formation and use of the polymer of this invention.

Aliphatic dicarboxylic acids, as the term is used herein, refer to carboxylic acids having two carboxyl groups each of which is attached to a saturated carbon atom. If the carbon atom to which the carboxyl group is attached is saturated and is in a ring, the acid is cycloaliphatic.

Aromatic dicarboxylic acids, as the term is used herein, are dicarboxylic acids having two carboxyl groups each of which is attached to a carbon atom in an isolated or fused benzene ring system. It is not necessary that both functional carboxyl groups be attached to the same aromatic ring and where more than one ring is present, they can be joined by aliphatic or aromatic divalent radical such as -O- or -SO<sub>2</sub>-.

Preferred aliphatic acids are cyclohexene dicarboxylic acids, sebacic acid, glutaric acid and adipic acid.

Preferred dicarboxylic acids for the preparation of the polyetherimide esters of the present invention are the aromatic dicarboxylic acids, mixtures thereof and mixtures of one or more dicarboxylic acids with an

aliphatic and/or cycloaliphatic dicarboxylic acid, most preferably the aromatic dicarboxylic acids. Among the aromatic acids those with 8-16 carbon atoms are preferred, particularly the benzene dicarboxylic acids, i.e., phthalic, terephthalic and isophthalic acids and their dimethyl derivatives. Especially preferred is dimethyl terephthalate.

5 Finally, where mixtures of dicarboxylic acids are employed in the practice of the present invention, it is preferred at that least about 60 mole %, preferably at least 80 mole %, based on 100 mole % of dicarboxylic acid (ii) be the same dicarboxylic acid or ester derivative thereof.

The polyetherimide ester polymers of the present invention may be prepared by a one-pot synthesis involving the reaction of the diol (i), the dicarboxylic acid (ii), the high molecular weight poly(oxy alkylene)-  
10 diamine (iii)(a)(1), and the tricarboxylic acid or its derivative (iii)(a)(2). In such a synthesis the polyoxal-  
kylene diimide diacid (iii)(b) is formed in-situ by the reaction of the poly(oxy alkylene)diamine with the tricarboxylic acid.

The poly(oxy alkylene)diamines (iii)(a)(1) suitable for use in the present invention may be represented by the following general formula

15 I.  $\text{H}_2\text{N-G-NH}_2$

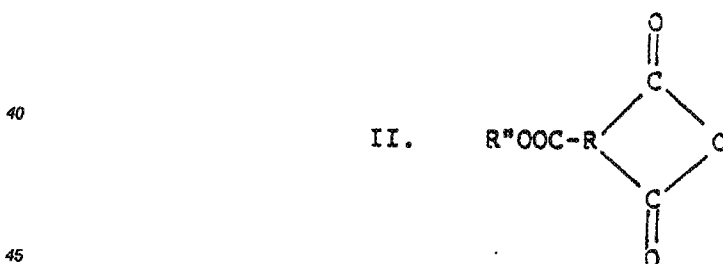
wherein G is the radical remaining after the removal of the amino groups of a long chain alkylene ether diamine. These polyether diprimary diamines are available commercially from Texaco Chemical Company under the trademark JEFFAMINE. In general they are prepared by known processes for the amination of glycols. For example, they may be prepared by aminating the glycol in the presence of ammonia, Raney  
20 nickel catalyst and hydrogen as set forth in Belgium Pat. No. 634,741. Alternatively, they may be prepared by treating glycol with ammonia and hydrogen over a Nickel-Copper-Chromium catalyst as taught by U.S. Patent No. 3,654,370. Other methods for the production thereof include those taught by U.S. Patent Nos. 3,155,728 and 3,236, 895 and French Nos. 1,551,605 and 1,466,708, all of the foregoing patents being incorporated herein by reference.

25 The long chain ether diamines suitable for use herein are the polymeric diamines having terminal (or as nearly terminal as possible) amine groups and an average molecular weight of from about 600 to about 12,000, preferably from about 900 to about 4,000. Additionally, the long chain ether diamines will generally have a carbon-to-oxygen ratio of from about 1.8 to about 4.3.

In general, the polyoxalkylene diamines useful in the practice of the present invention have an average  
30 molecular weight of from about 600 to about 12,000, preferably from about 900 to about 4,000.

The tricarboxylic acid (iii)(a)(2) may be almost any carboxylic acid anhydride containing an additional carboxylic group or the corresponding acid thereof containing two imide-forming vicinal carboxyl groups in lieu of the anhydride group. Mixtures thereof are also suitable. The additional carboxylic group must be esterifiable.

35 These tricarboxylic acid materials can be characterized by the following general formula



wherein:

50 R is a trivalent organic radical, preferably a C<sub>1</sub>-C<sub>20</sub> aliphatic or cycloaliphatic, or C<sub>6</sub>-C<sub>20</sub> aromatic trivalent radical;

R'' is preferably hydrogen or a monovalent organic radical which is preferably selected from C<sub>1</sub>-C<sub>6</sub> aliphatic and/or cycloaliphatic radicals and C<sub>6</sub>-C<sub>12</sub> aromatic radicals, e.g., phenyl, tolyl or benzyl; R' is most preferably hydrogen.

55 In the preparation of the instant polyetherimide ester polymers sufficient amounts of diol versus dicarboxylic acid, and tricarboxylic acid versus diamine must be present, as recognized in the art, to allow for substantially complete polymerization.

This type of one-pot reaction involving the reactions of (i) a diol component, (ii) a dicarboxylic acid

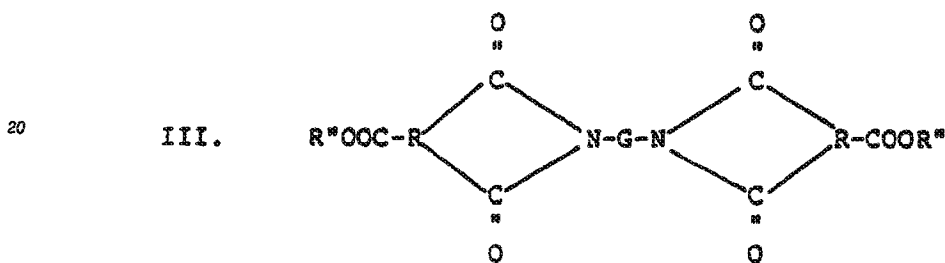
component, (iii)(a)(1) a poly(oxy alkylene)diamine component, and (iii)(a)(2) a tricarboxylic acid component is described in U.S. Patent No. 4,556,688 to McCready et al. incorporated herein by reference.

The amount by which the diamine (iii)(a)(1) and the dicarboxylic acid (ii) are used is generally not critical in forming the polyetherimide esters of the present invention. However, preferred amounts of the poly(oxy alkylene)diamine and dicarboxylic acid used are such that the weight ratio of the theoretical amount of the polyoxyalkylene diimide diacid, formable from poly(oxy alkylene)diamine and the tricarboxylic acid, to the dicarboxylic acid is from about 0.002 to 2.0:1, preferably from about 0.01 to 2.0:1, and more preferably from about 0.25 to 2.0, and most preferably from about 0.4 to 1.4. The actual weight ratio will be dependent upon the specific poly(oxy alkylene)diamine and tricarboxylic acid used and more importantly upon the desired physical and chemical properties of the resultant polyetherimide ester.

The instant polyetherimide esters may also be prepared by a two-pot synthesis involving the reaction of the diol (i), the dicarboxylic acid (ii), and the polyoxyalkylene diimide diacid (iii) (b). Such a reaction is described in U.S. Patent No. 4,556,705 to McCready, incorporated herein by reference.

The polyoxyalkylene diimide diacid (iii)(b) may be represented by the general formula

15



wherein G, R and R' are as defined hereinafore.

The polyoxyalkylene diimide diacids of Formula III suitable for use herein are high molecular weight diimide diacids having an average molecular weight greater than about 700, preferably greater than about 900. They may be prepared by the imidization reaction of one or more tricarboxylic acids (iii)(a)(2) containing two vicinal carboxyl groups or an anhydride group and an additional carboxyl group which must be esterifiable with the high molecular weight poly(oxy alkylene)diamine (iii)(a)(1). These polyoxyalkylene diimide diacids and processes for their preparation are disclosed in U.S. Patent No. 4,556,705, incorporated herein by reference.

In this two-pot process the amount of polyoxyalkylene diimide diacid and dicarboxylic acid utilized is generally not critical in forming the polyetherimide esters of the present invention. However, preferred amounts of the polyoxyalkylene diimide diacid and dicarboxylic acid are such that the weight ratio of the polyoxyalkylene diimide to the dicarboxylic acid is from about 0.002 to 2.01:1, preferably from about 0.01 to 2.01:1, more preferably from about 0.25 to 2.0:1, and most preferably from about 0.4 to 1.4:1.

It is also possible, as described in U.S. Patent No. 4,556,688, to prepolymerize the aromatic dicarboxylic acid and the diol to form a prepolyester, and then react this prepolyester with either the diimide diacid or with the tricarboxylic and the poly(oxy alkylene)diamine. Forming the prepolyester can be achieved by conventional esterification techniques such as those described in U.S. Patent Nos. 2,465,319 and 2,910,466, all of which are incorporated by reference.

In its preferred embodiment, the polyetherimide esters of the instant invention comprise the reaction products of dimethylterephthalate, optionally with up to 40 mole percent of another dicarboxylic acid or its ester forming derivative; butane diol, optionally with another diol such as butene diol, hexanediol, or cyclohexane dimethanol; and either a poly(oxy alkylene)diamine having an average molecular weight of from about 600 to about 12,000, preferably from about 900 to about 4,000, and trimellitic anhydride, or a polyoxyalkylene diimide diacid.

The instant polyetherimide esters may be prepared by conventional esterification/condensation reactions for the production of polyesters. These processes are described, inter alia, in U.S. Patents Nos. 3,763,109; 3,851,014; 3,801,547; 4,556,705, and 4,556,688, all of which are incorporated herein by reference.

The polyetherimide esters of the instant invention contain at least the following two recurring structural units:



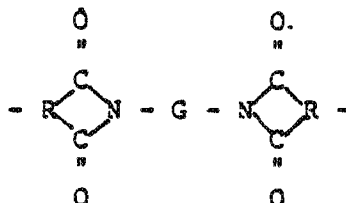


and



wherein:

A is the residue of the polyoxyalkylene diimide diacid absent the two carboxyl groups, i.e.,

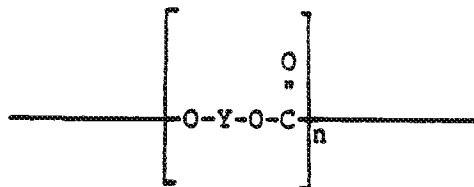


R<sup>1</sup> is the residue of the dio absent the two hydroxyl groups,  
R<sup>2</sup> is the residue of the dicarboxylic acid absent the two carboxyl groups, and  
G is as defined hereinafter.

Additionally, while not prepared, it is customary and preferred to utilize a catalyst or catalyst system in the process for the production of the present polyetherimide esters. These types of catalysts are set forth in U.S. Patent Nos. 4,556,705 and 4,566,688, both of which are incorporated herein by reference.

Both batch and continuous methods can be used for any stage of the ether imide ester polymer preparation. Polycondensation of the polyester prepolymer with the polyoxyalkylene diimide diacid can also be accomplished in the solid phase by heating finely divided solid polyester prepolymer with the diimide diacid in a vacuum or in a stream of inert gas to remove liberated low molecular weight diol. This method has the advantage of reducing degradation because it must be used at temperatures below the softening point of the prepolymer.

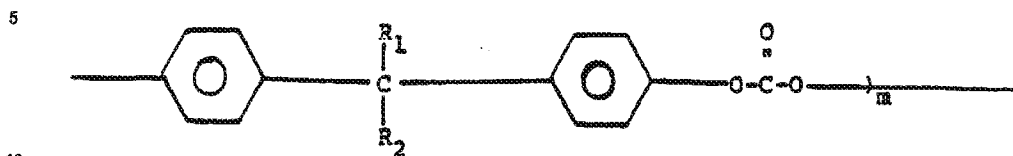
Polycarbonates suitable for use in the present invention are any of those known in the art. Especially preferred polycarbonates are high molecular weight, thermoplastic, aromatic polymers and include homopolycarbonates, copolycarbonates and copolyestercarbonates and mixtures thereof which have average molecular weights of about 8,000 to more than 200,000, preferably of about 20,000 to 80,000 and an I.V. of 0.30 to 1.0 dl/g as measured in methylene chloride at 25 C. In one embodiment, the polycarbonate are derived from dihydric phenols and carbonate precursors and generally contain recurring structural units of the formula;



where Y is a divalent aromatic radical remaining after removal of the hydroxy groups from the dihydric

phenol employed in the polycarbonate producing reaction, and  $n$  is greater than 1, preferably from about 10 to about 400.

Preferred polycarbonates resins are of the formula:



wherein  $R_1$  and  $R_2$  are independently hydrogen, (lower) alkyl or phenyl and  $m$  is at least 30 preferably between 40 and 300. The term (lower) alkyl includes hydrocarbon groups of from 1 to 6 carbon atoms.

Suitable dihydric phenols for producing polycarbonates include, for example,

2,2-bis(4-hydroxyphenyl)propane, bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 4,4-bis(4-hydroxyphenyl) heptane, 2,2-(3,5,3',5'-tetrachloro-4,4'-dihydroxyphenyl)propane, 2,2-(3,5,3',5'-tetrabromo-4,4'-dihydroxyphenyl)propane, and 3,3'-dichloro-4,4'-dihydroxydiphenylmethane.

Other dihydric phenols which are also suitable for use in the preparation of the above polycarbonates are disclosed in U.S. Patent Nos. 2,999,835; 3,038,365; 3,169,121; 3,334,154; and 4,131,575, incorporated herein by reference.

It is, of course, possible to employ two or more different dihydric phenols or a copolymer of a dihydric phenol with a glycol or with a hydroxy or acid terminated polyester, or with a dibasic acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in the preparation of the blends of the invention. Blends of any of the above materials can also be employed to provide the aromatic polycarbonate. In addition, branched polycarbonates such as are described in U.S. Patent No. 4,001,184, can also be utilized in the practice of this invention, as can blends of a linear polycarbonate and branched polycarbonate.

The carbonate precursor employed can be either a carbonyl halide, a carbonate ester or a haloformate. The carbonyl halides which can be employed are carbonyl bromide, carbonyl chloride and mixtures thereof. Typical of the carbonate esters which can be employed are diphenyl carbonate; a di(haloalkyl)carbonate such as di(trichlorophenyl) carbonate, di(tribromophenyl)carbonate, etc.; di(alkylphenyl) carbonate such as di(tolyl)carbonate, etc.; di(naphthyl)carbonate; di(chloronaphthyl)carbonate; etc., or mixtures thereof. The suitable haloformates include bis-haloformates of dihydric phenols (bischloroformates of hydroquinone, etc.) or glycols (bishaloformates of ethylene glycol, neopentyl glycol, polyethylene glycol, etc.). While other carbonate precursors will occur to those skilled in the art, carbonyl chloride, also known as phosgene, is preferred.

The polycarbonate may also be a copolyestercarbonate as described by Clayton B. Quinn in U.S. Patent 4,430,484 and Kenneth Miller in U.S. Patent No. 4,465,820. and the references cited therein, incorporated herein by reference. Preferred polyestercarbonates are those derived from the dihydric phenols and carbonate precursors described above and aromatic dicarboxylic acids or their reactive derivatives, such as the acid dihalides, e.g. dichlorides. A quite useful class of polyestercarbonates are the aromatic polyester carbonates derived from bisphenol A; terephthalic acid or isophthalic acid or a mixture thereof or their respective acid chlorides; and phosgene. If a mixture of terephthalic acid and isophthalic acid is employed, the weight ratio of terephthalic acid to isophthalic acid may be from about 2:8 to about 8:2.

The polycarbonates of the subject blends can be manufactured by known processes, such as, for example, by reacting a dihydric phenol with a carbonate precursor such as diphenyl carbonate or phosgene in accordance with methods set forth in the above-cited literature and U.S. Patent Nos. 4,018,750 and 4,123,436, or by transesterification processes such as are disclosed in the U.S. Patent No. 3,153,008, as well as other processes known to those skilled in the art. The aromatic polycarbonates are typically prepared by employing a molecular weight regulator, an acid acceptor and a catalyst. The molecular weight regulators which can be employed include phenol, cyclohexanol, methanol, alkylated phenols, such as octylphenol, parateriary-butyl-phenol, etc. Preferably, phenol or an alkylated phenol is employed as the molecular weight regulator.

The acid acceptor can be either an organic or an inorganic acid acceptor. A suitable organic acid acceptor is a tertiary amine and includes such materials as pyridine, triethylamine, dimethylaniline, tributylamine, etc. The inorganic acid acceptor can be one which can be either a hydroxide, a carbonate, a bicarbonate, or a phosphate of an alkali or alkaline earth metal.

The catalyst which can be employed are those that typically aid the polymerization of the monomer with phosgene. Suitable catalysts include tertiary amines such as triethylamine, tripropylamine, N,N-dimethylaniline, quaternary ammonium compounds such as, for example, tetraethylammonium bromide, cetyl triethyl ammonium bromide, tetra-n-heptylammonium iodide, tetra-n-propyl ammonium bromide, tetramethyl-ammonium chloride, tetra-methyl ammonium hydroxide, tetra-n-butyl ammonium iodide, benzyl-trimethyl ammonium chloride and quaternary phosphonium compounds such as, for example, n-butyl-triphenyl phosphonium bromide and methyltriphenyl phosphonium bromide.

Also included are branched polycarbonates wherein a polyfunctional aromatic compound is reacted with the monomer and carbonate precursor to provide a thermoplastic randomly branched polycarbonate. The polyfunctional aromatic compounds contain at least three functional groups which are carboxyl, carboxylic anhydride, haloformyl, or mixtures thereof. Illustrative polyfunctional aromatic compounds which can be employed include trimellitic anhydride, trimellitic acid, trimellityl trichloride, 4-chloroformyl phthalic anhydride, pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, benzophenonetetracarboxylic acid, benzophenonetetracarboxylic anhydride, and the like. The preferred polyfunctional aromatic compounds are trimellitic anhydride and trimellitic acid or their acid halide derivatives. Additionally, the polycarbonates resin/polyetherimide ester resin blend can contain other resin components.

Depending upon the needs of the individual practitioner of the invention, the blends of the present invention can contain one or more additional resin components, as long as such additional resin components are compatible with the basic polycarbonate resin/polyetherimide ester resin blended mixture. It has been discovered that the stabilizers of the present invention will still be effective in such blends that contain additional resin components. One example of an additional resin component that is compatible with the original blended mixture is a poly(alkylene terephthalate) resin. The preferred poly(alkylene terephthalate) resins are poly(butylene terephthalate) resin and poly(ethylene terephthalate) resin.

The ratio of polycarbonate resin to polyetherimide ester resin is not important to the present invention. However, preferably the ratio of polycarbonate resin component to polyetherimide ester resin component ranges from about 1:99 to about 99:1, and most preferably from about 10:90 to about 90:10.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the present invention, but are not intended to limit the scope of the claims in any manner whatsoever. All parts are by weight unless otherwise specified.

All compositions were prepared by melt blending the various components in a Prodex single screw extruder.

Examples 3 through 6 illustrate that the stabilizers of the present invention are effective when there is a third resin component in the polyetherimide ester/polycarbonate compositions; in the present instance, the third component was a poly(ethylene terephthalate).

Table I sets forth the composition of each of the Examples 1 through 8, inclusive. Table II sets forth the melting points for the polyetherimide ester resin component of each compositions and, where appropriate, the poly(ethylene terephthalate) component.

Examples 1, 3, 5 and 7 are outside the scope of the present invention and are the controls. Examples 2, 4, 6 and 8 illustrate the present invention.

TABLE I

Example	PEE	PC	PET	SDP
1	1000	4000	---	---
2	1000	4000	---	30
3	1000	3000	1000	---
4	1000	3000	1000	30
5	3000	1000	1000	---
6	3000	1000	1000	30
7	4000	1000	---	---
8	4000	1000	---	30

PEE is a polyetherimide ester resin having a modulus of 25,000.  
 PC is a poly(bisphenol A)carbonate.  
 PET is a poly(ethylene terephthalate).  
 SDP is a monosodium phosphate ( $\text{NaH}_2\text{PO}_4$ ).

TABLE II

Example	Melting Pt. (PEE) °C.	Melting Pt.(PET) °C.
1	195	---
2	201	---
3	199	250
4	202	253
5	203	247
6	206	252
7	205	---
8	206	---

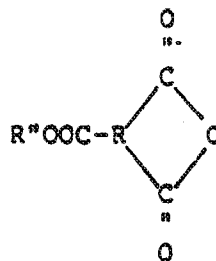
The stabilizing effect of the monosodium phosphate is demonstrated by the higher melting points of Examples 2, 4, 6 and 8 in comparison to their respective controls.

Obviously, other modifications and variations of the present invention are possible in light of the above teachings. It is, therefore, to be understood that changes may be made in the particular embodiments of the invention described which are within the full intended scope of the invention as defined by the appended claims. Obviously, flame retardants, stabilizers, fillers, and pigments can be advantageously employed by those skilled in the art in the present invention using conventional mixing methods.

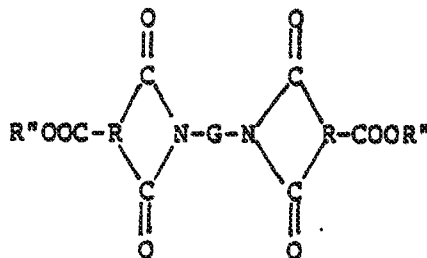
#### Claims

1. A thermoplastic composition comprising:
  - (a) at least one polycarbonate resin;
  - (b) at least one polyetherimide ester resin; and
  - (c) a melt-stabilizing amount of monosodium phosphate, monopotassium phosphate or a mixture thereof.
2. A composition as defined in claim 1 wherein the ratio of (a) to (b) ranges from about 1:99 to about 99:1.
3. A composition as defined in claim 2 wherein the ratio of (a) to (b) ranges from about 10:90 to about 90:10.
4. A composition as defined in claim 1 containing from above 0.01 to about 7.5 parts by weight of said phosphates per 100 parts by weight of (b).

5. A composition as defined in claim 4 containing from about .1 to about 4.0 parts by weight of said phosphate per 100 parts by weight of (b).
6. A composition as defined in claim 1 wherein component (c) is monosodium phosphate.
7. A composition as defined in claim 1 wherein said polycarbonate resin (a) is derived from a diphenol and phosgene or a phosgene precursor.
8. A composition as defined in claim 6 wherein said polycarbonate resin (a) is poly(bisphenol A carbonate).
9. The composition of claim 1 wherein said polyetherimide ester resin is comprised of the reaction products of:
- (a) at least one diol;
  - (b) at least one dicarboxylic acid or an ester forming reactive derivative thereof; and
  - (c) a set of reactants selected from
    - (1)(i) at least one high molecular weight poly(oxy alkylene)diamine, and (ii) at least one tricarboxylic acid or a derivative thereof; or
    - (2) at least one high molecular weight polyoxyalkylene diimide diacid.
10. The composition of claim 9 wherein said diol is a low molecular weight diol.
11. The composition of claim 9 wherein said diol has a molecular weight of about 250 or less.
12. The composition of claim 9 wherein said diol contains from 2 to about 15 carbon atoms.
13. The composition of claim 9 wherein said dicarboxylic acid or its derivatives is an aromatic dicarboxylic acid or its derivative.
14. The composition of claim 9 wherein (c) is (1).
15. The composition of claim 14 wherein said high molecular weight poly(oxy alkylene)diamine is represented by the formula
- $$\text{H}_2\text{N}-\text{G}-\text{NH}_2$$
- wherein G is the radical remaining after the removal of the amino groups of a long chain alkylene ether diamine.
16. The composition of claim 14 wherein said tricarboxylic acid or its derivative is represented by the formula



- wherein R is a C<sub>1</sub> to C<sub>20</sub> trivalent aliphatic, cycloaliphatic or aromatic radical, and R\* is hydrogen or a C<sub>1</sub>-C<sub>6</sub> aliphatic monovalent radical.
17. The composition of claim 9 wherein (c) is (2).
18. The composition of claim 17 wherein said high molecular weight polyoxyalkylene diimide diacid is represented by the formula

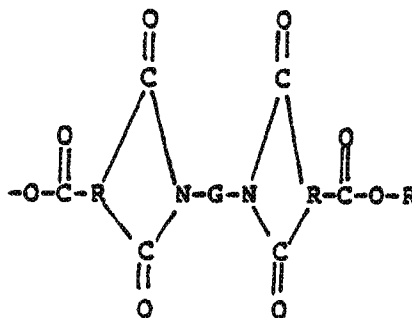


wherein:

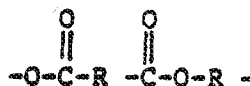
each R is independently selected from C<sub>1</sub>-C<sub>20</sub> aliphatic, cycloaliphatic or aromatic trivalent organic radicals; each R' is independently selected from hydrogen, C<sub>1</sub>-C<sub>6</sub> aliphatic or cycloaliphatic organic radicals, or C<sub>6</sub>-C<sub>12</sub> aromatic monovalent organic radicals; and

G is the radical remaining after the removal of the amino groups of a long chain alkylene ether diamine.

19. The composition of claim 1 wherein said polyetherimide ester resin is comprised of at least the following recurring structural units:



and



wherein:

R is the residue of a diol absent the two hydroxyl groups;

R' is the residue of a dicarboxylic acid absent the two carboxyl groups;

R<sup>2</sup> is a trivalent organic radical; and

G is the radical remaining after the removal of the amino groups of a long chain poly(oxy alkylene) diamine.

20. The composition of claim 19 wherein R is the residue of an aromatic dicarboxylic acid.

21. A composition as defined in claim 1 which also includes (b) an impact modifier resin.

22. A composition as defined in claim 1 which also includes a flame-retardant amount of a flame retardant additive or a combination of such additives.

23. The composition of claim 1 which further contains at least one additional resin component which is compatible to the polycarbonate/polyetherimide ester resin blend.

24. The composition of claim 23 wherein the one additional resin component is a poly(alkylene terephthalate) resin.

25. The composition of claim 24 wherein the poly(alkylene terephthalate) resin is poly(ethylene terephthalate).

26. The composition of claim 24 wherein poly(alkylene terephthalate) resin is poly(butylene terephthalate).



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number

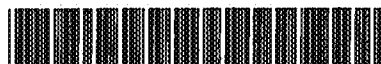
EP 89 11 6089

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 814 396 (N.-I. LIU) * claims; column 11, lines 6-12 *	1-3,7-20,22	C 08 L 69/00
Y	---	1-24,26	C 08 L 79/08
Y	EP-A-0 325 719 (GENERAL ELECTRIC CO.) * claims 1,5,12,13; page 7, lines 48,49 *	1-20,22	C 08 K 3/32 C 08 L 67/02 // (C 08 L 79/08 C 08 L 69:00 C 08 K 3:32 ) (C 08 L 79/08 C 08 L 69:00 C 08 L 67:02 C 08 K 3:32 )
Y	US-A-4 814 380 (N.-I. LIU) * claims 1-4,12-43; column 15, lines 41,64 *	1-3,7-24,26	
Y	US-A-4 532 290 (D.B.G. JAQUISS et al.) * claims 1,4-11,15; columns 3,4, examples * -----	1-24,26	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 L C 08 K
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 12-04-1990	Examiner VOIGTLAENDER R O J
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

(19)



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(11) Publication number:

**0 410 907 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 90420351.0

(51) Int. Cl.<sup>5</sup>: **C08K 13/02, C08L 67/02,**  
///(C08K13/02,3:32,5:00,5:37)

(22) Date of filing: 23.07.90

(30) Priority: 24.07.89 US 383467

(43) Date of publication of application:  
30.01.91 Bulletin 91/05

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GR

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(56) Thermoformed polyester articles.

- (97) Disclosed is a shaped, thin-walled, thermoformed, heat-set article, the composition of which comprises:
- a crystallizable polyester having repeating units from at least 90 mol % terephthalic acid and repeating units from at least 90 mol % 1,4-cyclohexanedimethanol, the total dicarboxylic acid mol % and the total glycol mol % each being 100 mol %, said polyester having an inherent viscosity of 0.7-1.1, and
  - a heat stabilizing amount of an antioxidant system comprising a hindered phenol, a thio ester or ether and a phosphate salt

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## THERMOFORMED POLYESTER ARTICLES

Technical Field

This invention relates to thermoformed, heat-set articles produced from high molecular weight polyesters containing repeating units from terephthalic acid and 1,4-cyclohexanedimethanol. The articles also  
 5 contain the combination of antioxidants as described herein.

Background of the Invention

10 There is presently a need for ovenable food trays capable of withstanding high temperatures. Most conventional home ovens are calibrated to only  $\pm 50^{\circ}\text{F}$  ( $10^{\circ}\text{C}$ ), and may reach temperature during use of up to  $450^{\circ}\text{F}$  ( $232^{\circ}\text{C}$ ). It is desirable that the containers do not lose impact strength, dimensional stability or discolor, so that they may be reused.

Normally, the ovenable containers are thermoformed from a polymeric material. In thermoforming, a  
 15 sheet of material is preheated to a temperature sufficient to allow the deformation thereof. The sheet is then made to conform to the contours of a mold by such means as vacuum assist, air pressure assist and matched mold assist. Thermoforming is a desirable method of producing thin wall articles.

Conventional materials used to produce thermoformed articles such as food trays include polymers such as polyethylene terephthalate. U.S. Patent No. 3,960,807 teaches a process for thermoforming articles  
 20 from a composition comprising a crystallizable polyester, a crack stopping agent and a nucleating agent. The crack stopping agent improves impact strength, and the nucleating agent provides faster crystallization. Crystallization is necessary to achieve high temperature stability.

Also of interest in U.S. Patent No. 4,463,121 which teaches thermoforming thin-walled articles from a composition consisting of polyethylene terephthalate, a polyolefin and optionally, a heat stabilizer such as a  
 25 hindered phenol. This patent teaches "higher molecular weights, as measured by increased intrinsic viscosities tend to display greater strength than lower molecular weight polyesters. When working with moderate and high molecular weight polyesters, higher crystallinity is used to increase tensile strength; however, flexural properties then diminish and the polyester becomes stiff and brittle. For any particular use of polyesters, therefore, the particular composition of materials and parameters must be carefully selected".  
 30 Certain phosphate salts are known stabilizers for vinyl polymers in which they act as acid acceptors. However, it is not believed to be known in the art that they are effective antioxidants for polyesters.

Applicants have now discovered that selected phosphate salts, namely  $\text{CaHPO}_4$ ,  $\text{Na}_2\text{HPO}_4$  and  $\text{K}_2\text{HPO}_4$ , provide improved thermo-oxidative stability to articles thermoformed from polyesters described herein. Applicants have discovered an article thermoformed from a high molecular weight polyester having  
 35 high tensile strength, yet having the ability to retain its flexibility and impact resistance when subjected to high oven temperatures. In these articles, it is necessary that the polyester contain repeating units from particular dicarboxylic acids(s) and a particular glycol, and have a high inherent viscosity indicating high molecular weight. In accordance with this invention, the article contains a heat stabilizer system which will prevent brittleness when subjected to high oven temperatures. Furthermore, articles thermoformed from the  
 40 polyesters in accordance with this invention retain their toughness even after being subjected to very low temperatures ( $-20^{\circ}\text{F}$ ) following being subjected to high oven temperatures of  $450^{\circ}\text{F}$  ( $232^{\circ}\text{C}$ ). Contrary to the teachings of the art with polyethylene terephthalate, crack stopping agents or impact strength-improving additives are not necessary with the present invention.

45

Disclosure of the Invention

It has now been found that certain phosphate salts, when used in combination with hindered phenols and thio ethers or esters provide stability comparable to that obtained using commercially available  
 50 phosphorous compounds such as phosphites.

According to the present invention, there is provided a shaped, thin-walled, thermoformed, heat-set article, the composition of which comprises:

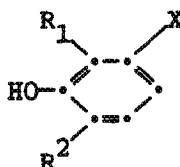
- a) a crystallizable polyester having repeating units from at least 85 mol % terephthalic acid and repeating units from at least 90 mol % 1,4-cyclohexanedimethanol, the total dicarboxylic acid mol % and the total glycol mol % each being 100 mol %, said polyester having an inherent viscosity (I.V.) of 0.7-1.1, and

b) a heat stabilizing amount of an antioxidant system comprising a hindered phenol, a thio ether or ester, and a phosphate salt.

Preferably, the polyesters may also contain up to 15 mol % repeating units from isophthalic acid. The polyester may also be modified with small amounts (less than 10%) of other conventional dicarboxylic acids and aliphatic or alicyclic glycols. Other dicarboxylic acids which may be used include aliphatic, cycloaliphatic or aromatic acids having 2 to 20 carbon atoms, and aliphatic or cycloaliphatic glycols having 2 to 12 carbon atoms. These polyesters may be produced using conventional polyesterification procedures described, for example, in U.S. Patent Nos. 3,305,604 and 2,901,460 the disclosures of which are incorporated herein by reference. Of course, esters of the acids (e.g., dimethyl terephthalate) may be used in producing the polyesters. It is also very desirable in the present invention for the I.V. of the polyester to be high, i.e., in the range of 0.87-1.1. Preferably, the high I.V.'s are attained by melt phase polymerization followed by conventional solid state polymerization.

The polyesters described herein for use in producing thermoformed articles have high melting temperatures, but they tend to oxidize at the high temperatures which may be encountered by food trays. Thus, it is necessary to include a heat stabilizing amount of an antioxidant in the thermoforming compositions. In accordance with another aspect of this invention, a particular blend of a hindered phenol, a thio ether or thio ester, and a phosphate salt provide unexpected results when used as antioxidants with the particular polyester described herein. These materials are known, of course, as stabilizers, but the particular combination used by applicants is not believed to be suggested in the art. For example, U.S. Patent 4,483,121 discloses a number of such antioxidants useful in polyethylene terephthalate.

Hindered phenol antioxidants are also commercially available. One suitable hindered phenol is Irganox 1010 antioxidant, marketed by Ciba-Geigy. Its chemical name is tetrakis[methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] methane. These hindered phenols have the general formula



wherein  $R_1$  is a branched alkyl group containing 3-20 carbon atoms,  $R_2$  is H or a straight or branched alkyl group containing 1 to 20 carbon atoms, and X is an alkyl group or an electron donating group.

Other hindered phenols useful in the present invention include 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-5-triazine-2,4,6-(1H, 3H, 5H)trione; 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris-(2-hydroxyethyl)-S-triazine-2,4,6-(1H, 3H, 5H)trione; octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate; thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy)hydrocinnamate; N,N-hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate); 1,6-hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate); 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene; 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine; n-octadecyl 3,5-di-tert-butyl-4-hydroxyphenylacetate; 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H, 3H, 5H)trione; 2,2'-methylenebis(4-ethyl-6-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-tert-butylphenol); 4,4'-methylenebis(2,6-di-tert-butylphenol); 4,4'-thioabis(6-tert-butyl-o-cresol); 3:1 condensate of 3-methyl-6-tert-butylphenol and crotonaldehyde; 4,4'-butyldienebis(6-tert-butyl-m-cresol); 3,5-di-tert-butyl-4-hydroxybenzyl ether; 2,2'-oxamidobis ethyl-3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; stearyl  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; distearyl 3-methyl-4-hydroxy-5-tert-butylbenzyl malonate; 4,4'-propylmethylenebis(2-tert-butyl-5-methylphenol); 2,2'-propylmethylenebis(4,6-dimethylphenol); 2,2'-methylenebis(4,6-di-tert-butylphenol); 1,4-bis(3',5'-di-tert-butyl-4'-hydroxybenzyl)-2,3,5,6-tetramethylbenzene; 1,1-bis(3'-cyclohexyl-4'-hydroxyphenyl)cyclohexane; 2,6-bis(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-4-methylphenol; 2,4,6-tris(( $\beta$ -(3',5'-di-tert-butyl-4'-hydroxyphenyl)ethyl)-1,3,5-triazine; 2,4,6-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)phenol.

The useful thio ethers and thio esters include esters of thiodipropionic acid, preferably dialkyl thiodipropionate and distearyl thiodipropionate.

The useful phosphate salts include calcium phosphate ( $\text{CaHPO}_4$ ), sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ), and potassium phosphate ( $\text{K}_2\text{HPO}_4$ ), all of which are commercially available.

Preferably, the hindered phenol is used in amounts of 0.05-2% based on the weight of the article. The phosphate salt is present in an amount of 0.01 to 0.20% based on the weight of the article. The thiodipropionate may be present in an amount of 0.05-1.0% based on the weight of the article. These

antioxidants may be added to the polyester separately or as a mixture.

The addition of nucleating agents provide faster crystallization during thermoforming and thus provide for faster molding. Conventional nucleating agents such as fine particle size inorganic or organic materials may be used. Suitable nucleating agents include talc, titanium dioxide, calcium carbonate, polymers, etc.  
 5 Normally, nucleating agents are used in amounts varying from 0.01% to 20%, based on the weight of the article.

Other conventional additives such as pigments, dyes, plasticizers, various stabilizers, etc., may be used as desired.

Ordinary thermoforming techniques known to those skilled in the art may be used in producing the  
 10 articles of this invention. Generally, the technique consists of the following steps:

1. Forming a substantially amorphous sheet from the composition.
2. Preheating the sheet until it softens and positioning it over the mold.
3. Drawing the preheated sheet onto the heated mold surface.
4. Heatsetting the formed sheet by maintaining sheet contact against the heated mold for a sufficient  
 15 time period to partially crystallize the sheet.
5. Stripping the part out of the mold cavity.

The sheeting and film for use in the thermoforming process can be made by any conventional method. The most common method being by extrusion through a flat die. It is important that the sheet or film be quenched immediately after extrusion in order to minimize the extent of crystallization developed after  
 20 forming.

The term substantially amorphous as used herein shall mean a sheet having a level of crystallinity low enough to enable thermoforming of the sheet to be accomplished with satisfactory mold definition and part formation.

The preheating of the substantially amorphous sheet prior to positioning over the thermoforming mold is  
 25 necessary in order to achieve the very short molding times required for a viable commercial process. The sheet must be heated above its T<sub>g</sub> and below the point at which it sags excessively during positioning over the mold cavity.

This invention can be practiced by using any of the known thermoforming methods including vacuum assist, air assist, mechanical plug assist or matched mold. The mold should be preheated to a temperature  
 30 sufficient to achieve the degree of crystallinity desired. Selection of optimum mold temperature is dependent upon type of thermoforming equipment, configuration and wall thickness of article being molded and other factors.

Heatsetting is a term describing the process of thermally inducing partial crystallization of a polyester article without appreciable orientation being present. In the practice of this invention, heatsetting is achieved  
 35 by maintaining intimate contact of the film or sheet with the heated mold surface for a sufficient time to achieve a level of crystallinity which gives adequate physical properties to the finished part. It has been found that desirable levels of crystallinity should be 10 to 30 percent.

The heat set part can be stripped out of the mold cavity by known means for removal. One method, blowback, involves breaking the vacuum established between the mold and the formed sheet by the  
 40 introduction of compressed air. In commercial thermoforming operation and part is subsequently trimmed and the scrap ground and recycled.

Experience with lower I.V. (0.76 I.V.) polyethylene terephthalate, suggests that solid-stating to an I.V. of 1.00 would produce a copolyester having a molecular weight comparable to a .84 I.V. polystyrene terephthalate and should be significantly tougher when exposed to the high cooking temperatures of 450° F.  
 45 It has been found, unexpectedly, that in addition to increasing the toughness of the copolyesters used in the present invention at 450° F, this toughness is maintained at 0° F even after the tray has been used for cooking and subsequently frozen. This does not occur with high molecular weight polyethylene terephthalate. Furthermore, the toughness of the copolyesters used in the present invention are maintained to temperatures as low as -20° F.

50 The following examples are submitted for a better understanding of this invention.

Stabilizer/nucleator concentrates are prepared using a Brabender PlastiCorder mixer using 58.5% polypropylene as a carrier, 8.0% Irganox 1010 antioxidant (hindered phenol), 1.5% CaHPO<sub>4</sub> (phosphate salt), 12% distearyl thiodipropionate, and 20% titanium dioxide as a nucleator. A pellet-to-pellet blend is then prepared using polyester and concentrate. The polyester used is Polyester A which has an I.V. of 0.95,  
 55 and has repeat units from 95 mol % terephthalic acid, 5 mol % isophthalic acid and 100 mol % 1,4-cyclohexanedimethanol. Extruded films (~25-30 mil) are then prepared from the blend using a Brabender extruder with a mixing screw. The films are cut into 3 X 12 inch pieces and the pieces are precrystallized at 175° C for 10 minutes (to avoid distortion of the film during oven aging). The films are placed on a rotating

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carousel in a forced-air oven at 400 and 450° F for intervals up to 90 minutes. The color change of the aged samples is measured using a Gardner Colorimeter. The relative brittleness of the samples is determined by flexing the samples manually through a 180 degree radius. All examples except Example 1 include 0.5% titanium dioxide. Examples 1-5 are controls. Example 6 is in accordance with this invention.

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Oven Aged at 450° F (232° C)									
Example		0 Min.		60 Min.		90 Min.			
		Color	Rating	Color	Rating	Color	Rating		
1. Polyester A		1	P	8	F	10	F		
2. Polyester A + 0.1% Hindered Phenol		2	P	8	F	9	F		
3. Polyester A + 0.1% Hindered Phenol + 0.3% DSTDP		1	P	2	P	3	F		
4. Polyester A + 0.1% Hindered Phenol + 0.1% Naugard P + 0.3% DSTDP		1	P	4	F	4	F		
5. Polyester A + 0.3% Hindered Phenol + 0.3% Naugard P + 0.3% DSTDP		2	P	5	P	6	F		
6. Polyester A + 0.2% Hindered Phenol + 0.04% CaHPO4 + 0.3% DSTDP		1	P	2	P	2	P		
P = Pass; film remained ductile									
F = Fail; film became brittle									
Color scale;									
1 = best									
10 = worst									

Example 6 shows the  $\text{CaHPO}_4$  is effective for stabilizing Polyester A against thermal breakdown and color change after oven aging at  $450^\circ\text{F}$  ( $232^\circ\text{C}$ ).

Whenever the term "inherent viscosity" (I.V.) is used in this application, it will be understood to refer to viscosity determinations made at  $25^\circ\text{C}$  using 0.5 gram of polymer per 100 ml of a solvent composed of 60 wt % phenol and 40 wt % tetrachloroethane.

Gardner CDM values are measured on a Gardner color difference meter using ASTM D-2244.

Materials referred to by trademark are described as follows:

Irganox 1010 antioxidant (hindered phenol) - tetrakis(methylene-3-(3,5-ditertiary butyl-4-hydroxyphenyl)propionate methane

Naugard P antioxidant -[tris(nonylphenyl) phosphite]

DSTDP - distearyl thiodipropionate

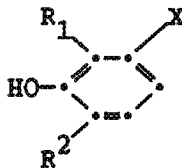
The "melting point" ( $T_m$ ) of the polymers described in this application are readily obtained with a Differential Scanning Calorimeter.

Unless otherwise specified, all parts, percentages, ratios, etc., are by weight.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

## Claims

1. A shaped, thin-walled, thermoformed, heat-set article, the composition of which is characterized as containing:
  - a) a crystallizable polyester having repeating units from at least 85 mol % terephthalic acid and repeating units from at least 90 mol % 1,4-cyclohexanedimethanol, the total dicarboxylic acid mol % and the total glycol mol % each being 100 mol %, said polyester having an inherent viscosity of 0.7-1.1, and
  - b) a heat stabilizing amount of an antioxidant system comprising a hindered phenol, a thio ether or ester and a phosphate salt.
2. The article according to Claim 1 wherein said polyester contains repeating units from 85-100 mol % terephthalic acid, repeating units from 15.0 mol % isophthalic acid and repeating units from substantially 100 mol % 1,4-cyclohexanedimethanol.
3. The article according to Claim 1 wherein said polyester has an inherent viscosity of 0.87-1.1.
4. The article according to Claim 1 which further comprises 0.01% to 20%, based on the total weight of the article, of a nucleating agent.
5. The article according to Claim 1 wherein said antioxidant comprises 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene or tetrakis(methylene-3-(3,5-ditertiary butyl-4-hydroxyphenyl)propionate methane.
6. The article according to Claim 1 wherein said antioxidant comprises a hindered phenol of the general formula



- wherein  $R_1$  is a branched alkyl group containing 3-20 carbon atoms,  $R_2$  is H or a straight or branched alkyl group containing 1 to 20 carbon atoms, and X is an alkyl group or an electron donating group.
7. An article according to Claim 1 wherein said antioxidant comprises
    - a) 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene,
    - b) calcium phosphate, sodium phosphate or potassium phosphate, and
    - c) di-lauryl thiodipropionate or di-stearyl thiodipropionate.
  8. An article according to Claim 1 wherein said antioxidant comprises
    - a) tetrakis(methylene 3-(3,5-ditertiary butyl-4-hydroxyphenyl) propionate methane,
    - b) calcium phosphate, sodium phosphate or potassium phosphate, and

c) di-lauryl thiodipropionate or di-stearyl thiodipropionate.

9. A shaped, thin-walled, thermoformed, heat-set article, the composition of which is characterized as containing:

- 5 a) a crystallizable polyester having repeating units from 90.99 mol % terephthalic acid, repeating units from 10-1 mol % isophthalic acid and substantially 100 mol % 1,4-cyclohexanedimethanol, the total dicarboxylic acid mol % and the total glycol mol % each being 100 mol %, said polyester having an inherent viscosity of 0.87-1.1,
- b) 0.05-2.0%, based on the total weight of the article, of an antioxidant system which consists essentially of
  - 10 1) a hindered phenol selected from the group consisting of 1,3,5-trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxybenzyl)benzene or tetrakis(methylene-3-(3,5-di-tertiary butyl-4-hydroxyphenyl)propionate methane,
  - 2) calcium phosphate, sodium phosphate, or potassium phosphate
  - 3) dilauryl thiodipropionate or distearyl thiodipropionate, and c) 0.01% to 20%, based on the total
- 15 weight of the article, of a nucleating agent.

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European Patent  
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## EUROPEAN SEARCH REPORT

Application Number

EP 90 42 0351

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	WO-A-8801285 (EASTMAN KODAK COMPANY) * page 6, lines 4 - 20; claims *	1-9	C08K13/02 C08L67/02 //(C08K13/02, 3:32,5:00,5:37 )
Y	US-A-3816377 (YUZI OKUZUMI) * column 3, line 49 - column 4, line 30 * * column 5, lines 30 - 37; claims *	1-9	
A	EP-A-78238 (CIBA-GEIGY AG) * page 11, lines 6 - 12; claims *	1	
A	EP-A-186011 (BASF AKTIENGESELLSCHAFT) * claims *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08K C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31 OCTOBER 1990	Examiner DE LOS ARCOS Y E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons * * * * * A : member of the same patent family, corresponding document	

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